
Computational Developments in Generalized Valence Bond Calculations

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ABSTRACT

In this article a procedure for generating starting orbitals for generalized valence bond (GVB) calculations is presented. This is achieved by selecting orbitals which correspond to specific bonds or electron pairs. These orbitals can be identified from the localized molecular orbitals, for both occupied and virtual orbitals, which are obtained through a unitary transformation of the Hartree-Fock canonical molecular orbitals using the Boys's localization method. A scheme has also been implemented which achieves optimum convergence of the pairwise orbital optimization. An object-oriented GVB program is developed which automatically generates reliable initial GVB orbitals, leading to proper and fast convergence. © 1996 by John Wiley & Sons, Inc.

Introduction

The Hartree-Fock (HF) single-determinantal wave function can be easily applied to describe many molecular properties well. However, the HF wave function, which consists of doubly occupied molecular orbitals, fails at describing bond dissociation correctly, for example. For systems or processes in which electron correlation plays an important role, HF theory can result in significant errors. The simple wave function that removes these deficiencies, while retaining proper spin symmetry, is the generalized valence bond (GVB) wave function, which was first proposed in

its most complete form by Goddard.¹ GVB calculations have been used in many areas,²⁻⁵ and they have been proven especially advantageous for studying excited states² and photodissociation pathways³ which cannot generally be described in terms of a single determinant of doubly occupied orbitals. De Maré et al.⁴ have successfully applied the GVB method to investigate the photochemistry of gaseous 1,3-butadiene and propene and their optimized structures.

The GVB wave function is a special case of multiconfiguration self-consistent field (MCSCF) methods,⁶ in which each pair of electrons is described by two or more self-consistently optimized orbitals. One advantage of the GVB approach is that, like SCF calculations, it does not require an integral transformation. Another advantage of the

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GVB wave function is that the GVB orbitals resemble the classical chemically bonded structures (e.g., with localized bonds and lone pairs⁷). A further advantage is that the energy gradients can be obtained analytically allowing for the gradient optimization of geometries. This makes it possible to calculate, for example, dipole moments,⁴ force constants, and fundamental frequencies, at equilibrium structures with the inclusion of electron correlation.⁸ However, one difficulty with the GVB method is that, unlike the HF method, it cannot be used as a "blackbox." For GVB calculations, molecular orbitals must be correctly paired using some initial molecular orbitals. Even when the orbital pairing is correct, GVB convergence is, in general, very poor compared to HF. Recently, Goddard et al.⁹ have significantly improved GVB convergence using the direct inversion of the iterative subspace (DIIS) technique and a special GVB orbital guess. Ionova and Carter¹⁰ presented an approach based on applying the DIIS directly to the GVB-PP orbitals, showing a better performance in convergence than the previously proposed scheme of applying DIIS to a series of composite Fock matrices.⁹ A reliable initial guess is required to ensure that the GVB calculation is within the DIIS radius of convergence. Although fast convergence is important, a correct initial guess is essential to ensure convergence on the correct state, especially for distorted geometries. Pulay et al. used the natural orbitals of the unrestricted Hartree-Fock wave function for generating starting orbitals for GVB and MCSCF calculations.⁸ Goddard et al.¹¹ developed a procedure for constructing initial GVB orbitals by localizing pseudo-Hartree-Fock (P-HF) molecular orbitals based on the SCF orbitals of the individual atoms. In their approach, the occupied P-HF orbitals are projected on atomic basis functions for GVB first natural orbitals, and the unoccupied HF orbitals are projected for GVB second natural orbitals.

The pseudospectral (PS) numerical method for SCF calculations has recently been extended for use in GVB calculations by Goddard et al.¹² In the restricted configuration interaction (RCI) approach,¹³ the PS integration method is combined with a contraction procedure to reduce the cost of two-electron integral evaluation and the length of CI expansions generated from a GVB reference. Murphy and Messmer⁶ developed a GVB wave function expression in terms of local nonorthogonal orbitals, in which GVB perfect-pairing (PP) spin couplings are relaxed to allow the local spatial orbitals to correspond to different spin

couplings (GVB/R). Nearly all of the correlation energy contained in a corresponding complete-active-space (CASSCF) expansion can be represented by a GVB/R wave function.

Previous studies¹⁴ have shown that GVB orbitals are highly localized and very similar to the localized molecular orbitals (LMOs) obtained using the Boys's criterion,¹⁵ for example. The GVB orbitals are, however, obtained by a rigorous energetic localization technique, whereas the Boys's LMOs are obtained by a maximal separation of centroids of charge through a unitary transformation of the HF orbitals. Generally, for a closed-shell system with N electrons, a full GVB-PP wave function involves a set of $N/2$ localized occupied orbitals and $N/2$ localized virtual orbitals, which are self-consistently optimized for electron correlation. The qualitative orbital view of molecules derived from *ab initio* GVB calculations leads to simple concepts involving structure, bond energies, and ordering of electronic states.⁷

In the GVB-PP scheme, each pair of electrons is described by two orbitals, which can be considered as the bonding and antibonding (or virtual) orbitals. Since these two GVB orbitals correspond to a specific bond (or lone pair), a correlation energy contribution can be associated with that electron pair. When performing GVB calculations, the PP orbitals are either set by some arbitrary default or selected by carefully pairing specific orbitals. If delocalized canonical molecular orbitals (CMOs) are used as the initial GVB orbitals, it is impossible to identify these in terms of specific bonds or lone pairs, and the resulting orbitals may not represent the lowest energy solution. In our scheme, initial GVB-PP orbitals which correspond to specific chemical bonds are generated automatically. A procedure to get optimum convergence for pairwise orbital optimization is also described in this work. Our GVB program is written using the OSIPE (Open Structured Interfaceable Programming Environment)¹⁶ tools, on which the program MUNGAUSS¹⁷ is based. OSIPE is an object-oriented approach to programming in which objects are computed dynamically.

A brief summary of the GVB method is given in this article. Then we outline our procedure for the automatic generation of correct GVB-PP initial orbitals, followed by a description of our procedure for improving convergence of the pairwise orbital optimization. Finally, the results of GVB calculations on several systems, along with discussion of convergence and bond dissociation energies, are presented and compared with other

methods. A detailed study of GVB equilibrium geometries using our new GVB program is reported in a separate article.¹⁸

Summary of the GVB Method

THE GVB-PP WAVE FUNCTION

The HF wave function for a closed-shell singlet state is expressed by a single Slater determinant:

$$\Psi_{\text{HF}} = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \cdots \psi_n \bar{\psi}_n\rangle \quad (1)$$

A simple generalization is to allow selected electron pairs to be described by two or more self-consistently optimized orbitals. The result is the GVB wave function. The closed-shell orbital description of a singlet electron pair is replaced by a GVB pair consisting of two nonorthogonal orbitals coupled into a singlet.¹ In this GVB wave function, the strong orthogonality (SO) constraint requires that all orbitals, other than the two within a given singlet pair, be orthogonal. The general form of the GVB wave function is

$$\Psi_{\text{GVB}} = \mathcal{A}[\Psi_{\text{core}} \Psi_{\text{pair}} \Psi_{\text{open}}] \quad (2)$$

where \mathcal{A} is the antisymmetrizer. For a system with N electrons, $2N_{\text{core}}$ electrons are described with doubly occupied orbitals, and N_{open} electrons are high spin coupled ($S = N_{\text{open}}/2$).

$$\begin{aligned} \Psi_{\text{core}} &= \prod_{i=1}^{N_{\text{core}}} (\psi_i^c \alpha)(\psi_i^c \beta) \quad \text{and} \\ \Psi_{\text{open}} &= \prod_{i=1}^{N_{\text{open}}} (\psi_i^o \alpha) \end{aligned} \quad (3)$$

where ψ_i^c , ψ_i^o are orthogonal spatial orbitals. The Ψ_{pair} can be constructed in a number of ways depending on the choice of the spin coupling. In the perfect-pairing spin-coupling procedure, the singlet is coupled by pairs of orbitals (ψ_{1i}^s, ψ_{2i}^s) with spin functions

$$\Theta_{\text{PP}} = \prod_{i=1}^{N_{\text{pair}}} (\alpha\beta - \beta\alpha)$$

where $N_{\text{pair}} = (N - N_{\text{open}})/2 - N_{\text{core}}$. The GVB wave function, in which the perfect pairing and strong orthogonality restrictions are both imposed, is referred to as the GVB-PP wave function and is

given as

$$\Psi_{\text{pair}} = \prod_{i=1}^{N_{\text{pair}}} (\psi_{1i}^s \psi_{2i}^s + \psi_{2i}^s \psi_{1i}^s)(\alpha\beta - \beta\alpha) \quad (4)$$

where ψ_{1i}^s, ψ_{2i}^s are the GVB orbitals in pair i , with $\langle \psi_{1i}^s | \psi_{2i}^s \rangle = S_i$. Computationally, it is more convenient to use orthogonal orbitals. The nonorthogonal GVB orbitals ψ_{1i}^s, ψ_{2i}^s can be replaced by the orthogonal orbitals ψ_{1i}, ψ_{2i} through the following transformation:

$$\begin{cases} \psi_{1i}^s = (\sigma_{1i} + \sigma_{2i})^{-\frac{1}{2}} (\sigma_{1i}^{\frac{1}{2}} \psi_{1i} + \sigma_{2i}^{\frac{1}{2}} \psi_{2i}) \\ \psi_{2i}^s = (\sigma_{1i} + \sigma_{2i})^{-\frac{1}{2}} (\sigma_{1i}^{\frac{1}{2}} \psi_{1i} - \sigma_{2i}^{\frac{1}{2}} \psi_{2i}) \\ \langle \psi_{1i} | \psi_{2i} \rangle = 0 \\ \sigma_{1i}^2 + \sigma_{2i}^2 = 1, \quad \text{and} \quad \sigma_{1i}, \sigma_{2i} > 0 \end{cases} \quad (5)$$

Under such a transformation, each GVB-PP orbital in Eq. (4) is replaced by

$$\begin{aligned} &(\psi_{1i}^s \psi_{2i}^s + \psi_{2i}^s \psi_{1i}^s)(\alpha\beta - \beta\alpha) \\ &\rightarrow (\sigma_{1i} \psi_{1i} \psi_{1i} - \sigma_{2i} \psi_{2i} \psi_{2i})(\alpha\beta - \beta\alpha) \end{aligned} \quad (6)$$

For a two-electron system, this GVB wave function is identical to the simple two configuration MC-SCF wave function

$$\Psi_{\text{MCSCF}} = C_A |\psi_{1i} \bar{\psi}_{1i}\rangle + C_B |\psi_{2i} \bar{\psi}_{2i}\rangle \quad (7)$$

where C_A, C_B are configuration coefficients to be optimized. The natural orbital pairs (ψ_{1i}, ψ_{2i}) are generally well localized and can be easily identified with specific bonds or electron pairs, where ψ_{1i} can be associated with the bonding type orbital and ψ_{2i} with an antibonding type orbital.

Using the orthogonal GVB orbitals, the energy expression for the GVB-PP wave function becomes similar to the HF expression

$$E = 2 \sum_{i=1}^{N_{\text{occ}}} f_i h_{ii} + \sum_{i,j=1}^{N_{\text{occ}}} (a_{ij} J_{ij} + b_{ij} K_{ij}) \quad (8)$$

where N_{occ} is the number of the occupied orbitals and the standard definitions for the one-electron (h_{ii}), Coulomb (J_{ij}), and exchange (K_{ij}) energies are used.¹ The orbital occupation coefficients f_i and the two-electron coupling coefficients a_{ij}, b_{ij} ,

depend on the GVB wave function, and their definition is given in ref. 1.

PAIRWISE ORBITAL OPTIMIZATION

The general condition for the optimum orbitals, corresponding to the energy expression given by Eq. (8), is that the first-order change in the energy due to changes in the orbitals is zero, leading to

$$\sum_i \langle \delta \psi_i | F_i | \psi_i \rangle = 0 \quad (9)$$

where F_i is the Fock operator for the orbital ψ_i , and

$$F_i = f_i h + \sum_j^{N_{\text{occ}}} (a_{ij} J_j + b_{ij} K_j) \quad (10)$$

where h is the one-electron operator and J_j , K_j are the Coulomb and exchange operators.¹ The energy expression can be written as

$$E = \sum_i [f_i h_{ii} + \langle \psi_i | F_i | \psi_i \rangle] \quad (11)$$

For the optimal orbitals ψ_i and ψ_j , the variational condition is

$$\langle \psi_i | (F_i - F_j) | \psi_j \rangle = 0 \quad (12)$$

Because the Fock operator depends on the orbitals, the variational equations must be solved iteratively.

In the iterative procedure, the orbitals are optimized with respect to each other. The independent pairwise optimization allows mixing between only two orbitals at a time, so that

$$\begin{cases} \psi'_i = (\psi_i + \lambda_{ij} \psi_j) / (1 + \lambda_{ij}^2)^{\frac{1}{2}} \\ \psi'_j = (\psi_j + \lambda_{ji} \psi_i) / (1 + \lambda_{ji}^2)^{\frac{1}{2}} \end{cases} \quad (13)$$

where λ_{ij} , λ_{ji} are orbital correction factors. Generally, since orbital orthonormality must always be preserved, these corrections cannot be fully independent and orbital orthogonality requires that $\lambda_{ji} = -\lambda_{ij}$. In keeping with the variational condition that the matrix elements $A_{ij} = \langle \psi_i | (F_i - F_j) | \psi_j \rangle$ must be zero, under the second-order approximation,¹ the orbital correction factors

are given as

$$\lambda_{ij} = \frac{\langle \psi_i | F_j - F_i | \psi_j \rangle}{\langle \psi_i | (F_j - F_i) | \psi_i \rangle - \langle \psi_j | (F_j - F_i) | \psi_j \rangle + B_{ij}} \quad (14)$$

where $B_{ij} = 2(a_{ii} + a_{jj} - 2a_{ij})K_{ij} + (b_{ii} + b_{jj} - 2b_{ij})(J_{ij} + K_{ij})$.

Pairwise orbital optimization deals with the variation of only one variable at a time and is expected to converge to a solution directly (linearly) accessible through individual pairwise changes. In the pairwise orbital mixing scheme, once λ_{ij} has been determined, orbitals ψ_i , ψ_j are redefined before proceeding to the next pair. Because each mixing coefficient is determined in a completely independent way, this approach tends to have some oscillatory behavior. The simple procedure does, however, converge successfully. In addition to the foregoing orbital optimization, the GVB-CI coefficients [σ_{1i} , σ_{2i} in Eq. (6)] are optimized in terms of the GVB-PP pair energy contribution.¹

Generation of Initial GVB Orbitals

CMO INITIAL ORBITALS

One obvious choice for initial GVB orbitals is the use of canonical molecular orbitals, which, for example, can be generated from extended Huckel or HF calculations. With CMO it is possible, for a few cases, to select orbital pairs automatically which correspond to specific chemical bonds, using an identification matrix (\mathcal{J}). The identification matrix element $\mathcal{J}_{iA}^{\text{CMO}}$ for CMO, ψ_i centered on atom A is given by

$$\mathcal{J}_{iA}^{\text{CMO}} = \frac{\sum_{\mu \in A} (C_{\mu i})^2}{\sum_{\mu=1} (C_{\mu i})^2} \quad (15)$$

where the $C_{\mu i}$'s are the MO coefficients corresponding to ψ_i . From the identification matrix, a given ψ_i can be identified as corresponding to a specific bond or electron pair. For instance, at STO-3G the identification matrix elements for $\text{C}_2\text{H}_4(D_{2h})$ are $\mathcal{J}_{8A} = \mathcal{J}_{9A} = 0.50$, $A = \text{C}_1$ and C_2 , and $\mathcal{J}_{8A} = \mathcal{J}_{9A} = 0.00$, $A = \text{H}_1, \text{H}_2, \text{H}_3$, and H_4 . These results indicate that ψ_8 of ethylene is a (π) bonding orbital between the two carbon atoms, and ψ_9 is the corresponding (π) virtual (or antibonding) orbital.

Generally, only for π bond orbitals (or some conjugated bonds) can perfect-pairing orbitals be automatically constructed from CMOs. It is difficult to choose the correct pairing for the σ bond orbitals from CMOs. On the other hand, LMOs are highly localized to atoms and can generally be characterized as specific bonds between two atoms.

LMO INITIAL ORBITALS

Since GVB orbitals are highly localized, a logical choice for initial GVB orbitals is the use of LMOs. However, if all the occupied orbitals are allowed to mix during the localization procedure, the resulting localized multiple bonds become equivalent. For example, the σ and π bonds in ethylene will transform into two equivalent bent bonds.

This problem can be easily overcome by classifying the orbitals into different localization groups, which are defined by the MO selection vector \mathcal{S} . The default for \mathcal{S} is two sets of orbitals (one for occupied, and another for virtual):

$$\mathcal{S}_i = \begin{cases} 1 & \text{if } i \text{ is an occupied orbital} \\ 2 & \text{if } i \text{ is a virtual orbital} \end{cases} \quad (16)$$

For example, the default for C_2H_4 at STO-3G is $\mathcal{S} = (1111111222222)$. In this case, the first eight occupied CMOs are localized as one group, and the last six virtual CMOs are localized as a second group. When symmetry is used to separate the σ and π bonds, the MO selection vector \mathcal{S} becomes (11111113422222), where the π , π^* orbitals (ψ_8 and ψ_9) are not transformed.

In general, with the MO selection vector \mathcal{S} , it is possible to modify the default using a simple menu command¹⁶ and thus to select any number of localization groups:

$$\mathcal{S}_i \begin{cases} 2 + j & \text{if } i \text{ is a selected occupied orbital} \\ 2 + N_g + j & \text{if } i \text{ is a selected virtual orbital} \end{cases} \quad (17)$$

with $j = 1$ for the first group of selected orbitals and $j = N_g$ for last one, where N_g is the total number of selected groups. In this way, the CMOs can be divided into a total of $2 + 2 \times N_g$ groups for localization. By default, the σ and π orbitals are transformed separately resulting in $\sigma\pi$ bonds as opposed to banana bonds.

The two bent bond description of ethylene is more suitable for describing the dissociation of the $\text{C}=\text{C}$ bond of ethylene into two methylenes with two equivalent bent bonds. However, it is not

suitable for describing rotation about the $\text{C}=\text{C}$ double bond, where twisting of the π bond results in two nonequivalent bonds. Schultz and Mesmer¹⁹ have shown that the bent bond description is energetically favoured over the $\sigma\pi$ description at the GVB level for a number of molecules, including C_2H_4 . However, our GVB-PP results demonstrate that the $\sigma\pi$ description of the $\text{C}=\text{C}$ double bond is energetically favored over the bent bond description at the equilibrium geometry, which is in agreement with Carter and Goddard's results²⁰ for $\text{F}_2\text{C}=\text{CF}_2$.

CHARACTERIZING BONDING ORBITALS

Initial orbitals corresponding to specific bonds can be generated from the LMOs, which are obtained through a unitary transformation of the CMOs using the Boys's localization method¹⁵ for both occupied and virtual orbitals. The localization procedure is carried out in terms of the MO selection vector \mathcal{S} . The LMO coefficient matrix (\mathbf{L}) and CMO coefficient matrix (\mathbf{C}) are related by the transformation matrix (\mathbf{T}) as $\mathbf{L} = \mathbf{C}\mathbf{T}$.

Similar to Eq. (15), the LMO identification matrix (\mathcal{S}^{LMO}) is defined as

$$\mathcal{S}_{iA}^{\text{LMO}} = \frac{\sum_{\mu \in A} (L_{\mu i})^2}{\sum_{\mu=1} (L_{\mu i})^2} \quad (18)$$

where $0.00 \leq \mathcal{S}_{iA} \leq 1.00$ and $\sum_A \mathcal{S}_{iA} = 1.00$. Using the LMO identification matrix, one can construct a binary type matrix \mathcal{B} with matrix elements defined as

$$\begin{cases} \mathcal{B}_{iA} = 0, & \text{if } \mathcal{S}_{iA} \leq \epsilon \\ \mathcal{B}_{iA} = 1, & \text{if } \mathcal{S}_{iA} > \epsilon \end{cases} \quad (19)$$

where ϵ is a threshold. The threshold is initially set at $\frac{1}{3}$ and is then decreased by increments (e.g., 0.03) until two bonding atoms are found or the minimum threshold (e.g., 0.10) is reached. Using this scheme, the matrix elements \mathcal{B}_{iA} are determined for all doubly occupied and virtual orbitals. The $\mathcal{B}_{iA} = \mathcal{B}_{iB} = 1$ indicates that LMO ψ_i^{LMO} corresponds to a bond between atoms A and B.

PERFECT PAIRING

With the binary matrix \mathcal{B} , the selection of GVB perfect-pairing orbitals becomes straightforward and automatic. For the occupied ψ_i^{LMO} , which has

been identified as a bond between atoms A and B, the corresponding ψ_i^{LMO} can be found using the following criterion:

$$\mathcal{B}_{iA} = \mathcal{B}_{jA}, \quad \text{for all atoms } A \quad (20)$$

If more than one virtual orbital satisfies this criterion, the following additional condition is used:

$$\left| \sum_{\mu \in A} L_{\mu i} L_{\mu j} - \sum_{\mu \in B} L_{\mu i} L_{\mu j} \right| = \text{Maximum} \quad (21)$$

The result is the perfect-pairing orbitals (ψ_i^{LMO} and ψ_j^{LMO}) associated with the A-B bond. The initial GVB pair function ψ_{A-B} corresponding to the A-B bond can be constructed as in Eq. (6), using the pairing orbitals.

$$\psi_{A-B} = (\sigma_i \psi_i^{\text{LMO}} \psi_i^{\text{LMO}} - \sigma_j \psi_j^{\text{LMO}} \psi_j^{\text{LMO}}) \times (\alpha\beta - \beta\alpha) \quad (22)$$

INITIAL GUESS

Our program can handle a number of different cases for the initial GVB orbitals: (1) Automatically generate LMO PP orbitals for all bonds (with frozen cores). (2) Generate LMO PP orbitals for selected bonds. (3) Read the orbitals which can be obtained from previous GVB calculations or can be created by other methods. (4) Use an undistorted geometry to create GVB orbitals for a distorted geometry. (5) Generate GVB orbitals for open-shell cases. (6) Generate CMO PP orbitals automatically (for some cases) or from selected orbitals pairs. For (1) and (2) and LMOs may, in our current version, be generated from Huckel MOs or from converged HF MOs.

Orbital Optimization and Convergence

Our GVB procedure is carried out as illustrated in Figure 1. Before STEP 0, the OSIFE structure of the program¹⁶ ensures that all objects required for the GVB calculation have been built. For example, the initial orbitals are built by a call to function `getobj('MATSQG-COEFF-CMO-AO-GUESS-GVB')`.

ORBITAL OPTIMIZATION

Using the basis expansion $\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}$, where ϕ_{μ} are the atomic orbitals, the energy expression of

Eq. (11) can be written as

$$E = \sum_{\mu} \sum_{\nu} \sum_i C_{\mu i} * C_{\nu i} E_{i0} \quad (23)$$

where $E_{i0} = f_i h_{\mu\nu} + \langle \phi_{\mu} | E_i | \phi_{\nu} \rangle$.

The orbital coefficients $C_{\mu i}$ are redefined by Eq. (13), which can be expressed as an orbital rotation

$$\begin{cases} \psi'_i = \psi_i \cos \theta + \psi_j \sin \theta \\ \psi'_j = \psi_j \cos \theta - \psi_i \sin \theta \end{cases} \quad (24)$$

with

$$\cos \theta = \left(\frac{1}{1 + (\xi \lambda_{ij})^2} \right)^{\frac{1}{2}} \quad (25)$$

The pairwise orbital correction factor λ_{ij} is calculated using Eq. (14), and a scaling factor (ξ) is introduced to accelerate convergence. The scaling factor ξ is optimized to minimize E with E_{i0} fixed (cf. STEP 4 in Fig. 1). The default ξ is set to 1.00, and generally the optimized value is about 0.8. The rotation procedure is carried out simultaneously and with a single scaling factor for all orbitals. After the rotation the orbitals are orthogonalized by the Schmidt procedure.

CONVERGENCE ACCURACY

Three different convergence criteria are used to determine the optimization accuracy and ensure proper convergence of the GVB energy:

1. The orbital correction convergence criteria

$$\rho_{\text{orb}} = \left(\frac{\sum A_{ij}^2}{N_{\text{basis}} \times (N_{\text{basis}} + 1)/2 - N_{\text{basis}}} \right)^{\frac{1}{2}} \quad (26)$$

2. The orbital coefficients convergence criteria

$$\rho_c = \left(\frac{\sum_{\mu=1, N_{\text{basis}}} \sum_{i=1, N_{\text{occ}}} (C'_{\mu i} - C_{\mu i})^2}{N_{\text{basis}} \times N_{\text{occ}}} \right)^{\frac{1}{2}} \quad (27)$$

3. The density matrix convergence criteria ρ_d :

$$\rho_d = \frac{(\sum_{i,j=1, N_{\text{basis}}} (\mathbf{P}'_{ij} - \mathbf{P}_{ij})^2)^{\frac{1}{2}}}{N_{\text{basis}}} \quad (28)$$

where the density matrix \mathbf{P} is defined as $\mathbf{P} = \mathbf{COC}^+$, with \mathbf{O} being a diagonal matrix represent-

STEP 0 - Optimize CI coefficients σ_i using the initial orbitals.

STEP 1 - Construct the Fock matrix over AOs, $\langle \psi_i | F_i | \psi_j \rangle$ and $A_{ij} = \langle \psi_i | (F_i - F_j) | \psi_j \rangle$, where

$$F_i = f_i h + \sum_j^{N_{occ}} (a_{ij} J_j + b_{ij} K_j) \quad (10)$$

STEP 2 - Pairwise optimization of GVB-PP orbitals to get orbital correction factors λ_{ij} .

$$\lambda_{ij} = \frac{\langle \psi_i | F_j - F_i | \psi_j \rangle}{\langle \psi_i | (F_j - F_i) | \psi_i \rangle - \langle \psi_j | (F_j - F_i) | \psi_j \rangle + B_{ij}} \quad (14)$$

$$\text{where } B_{ij} = 2(a_{ii} + a_{jj} - 2a_{ij})K_{ij} + (b_{ii} + b_{jj} - 2b_{ij})(J_{ij} + K_{ij})$$

STEP 3 - Construct new orbitals.

$$\begin{cases} \psi'_i = \psi_i \cos \theta + \psi_j \sin \theta \\ \psi'_j = \psi_j \cos \theta - \psi_i \sin \theta \end{cases} \quad (24)$$

$$\text{where } \cos \theta = 1 / (1 + (\xi \lambda_{ij})^2)^{\frac{1}{2}}$$

STEP 4 - Minimize E with respect to ξ with E_{i0} fixed (Eq. (23)), go to STEP 5. If no minimum is found or the orbital corrections are large go to STEP 2.

STEP 5 - Extrapolate/Interpolate C .

STEP 6 - Recalculate coulomb and exchange integrals (J, K).

STEP 7 - Reoptimize CI coefficients only if ρ_c is small enough (e.g. ≤ 0.01).

STEP 8 - Calculate the energy.

$$E = 2 \sum_{i=1}^{N_{occ}} f_i h_{ii} + \sum_{i,j=1}^{N_{occ}} (a_{ij} J_{ij} + b_{ij} K_{ij}) \quad (8)$$

STEP 9 - Calculate the density matrix and check for convergence ($\rho_{orb}, \rho_c, \rho_d$).

- GO TO STEP 1

FIGURE 1. The main steps in the GVB iterative process.

ing the orbital occupancy, where

$$O_i = \begin{cases} 2 & \text{if } i \text{ is a core orbital} \\ 2\sigma_i^2 & \text{if } i \text{ is a GVB-PP orbital with coefficient } \sigma_i \\ 1 & \text{if } i \text{ is an open orbital} \end{cases} \quad (29)$$

The density matrix convergence criteria is impor-

tant since it incorporates convergence in both the orbital coefficients and the orbital occupancy or GVB-CI coefficients.

CI COEFFICIENTS AND EXTRAPOLATION

The GVB-CI coefficients in Eq. (22) are optimized at the initial orbitals and are only reopti-

mized when the change in the orbital coefficients is small enough. Pople's 3/4 point and Dewar's^{17c} extrapolation methods, which have been well studied for HF-SCF in MUNGAUSS,¹⁷ are available to extrapolate the orbital coefficients $C_{\mu i}$. In the default procedure, the 3/4 point method is used until the orbital correction is small enough, at which point we switch to Dewar's extrapolation method.

Results and Discussion

GVB RESULTS OF H₂O, C₂H₄, AND C₂H₆

H₂O

To compare with the previous *ab initio* calculations,⁶ the GVB calculations on H₂O are performed by using Dunning's double-zeta basis²¹ and Schaefer's CISD equilibrium geometry.²² The GVB(2/4) wave function of H₂O is constructed to correlate the two O-H bonds, while the O_{1s} and the two oxygen lone pairs are treated as closed-shell cores. The four H₂O GVB(4/8) orbitals consist of two equivalent O-H bonds and two equivalent nonbonding oxygen lone pairs. The GVB(4/8) wave function is

$$\Psi_{\text{H}_2\text{O}}^{\text{GVB}} = \mathcal{A}[\Psi_{\text{core}} \psi_{\text{O-H1}} \psi_{\text{O-H2}} \psi_{lp1} \psi_{lp2}] \quad (30)$$

where $\psi_{\text{O-H}}$, ψ_{lp} are GVB pair functions corresponding to the O-H bonds and the oxygen lone pairs, respectively [cf. Eq. (22)]. The results for the GVB calculations on H₂O are summarized in Table I. The correlation energy for GVB(4/8) has the relationship

$$\Delta E_{\text{total}} = 2\Delta E_{\text{O-H}} + 2\Delta E_{lp} \quad (31)$$

where $\Delta E_{\text{O-H}}$ represents the correlation energy contributed from an O-H bond pair and ΔE_{lp} represents the correlation energy contributed from an oxygen lone pair. Our GVB(4/8) result for ΔE_{total} is -0.0632 au, with $\Delta E_{\text{O-H}} = -0.022$ au and $\Delta E_{lp} = -0.009$ au, which is in good agreement with Goddard's values of -0.0642 au, -0.021 au, and -0.011 au for ΔE_{total} , $\Delta E_{\text{O-H}}$, and ΔE_{lp} , respectively.^{1b}

C₂H₄

For C₂H₄, GVB calculations are carried out with the 6-31G** basis set and the D_{2h} experimental

TABLE I.
Comparison of the GVB Results for H₂O
(energy in Hartrees).

Method ^a	Energy	Correlation Energy	
		This Work	Reference ^b
HF	-76.00984	—	—
GVB(1/2)	-76.03216	-0.02232	-0.0209
GVB(2/4)	-76.05415 ^c	-0.04421	-0.0418
GVB(4/8)	-76.07299	-0.06315	-0.0642

^aGVB(1/2): for an O-H1 bond. GVB(2/4): adding an O-H2 bond. GVB(4/8): adding two oxygen lone pairs.

^bGoddard et al., results from ref. 1b.

^cThe Messmer et al. SOPP approach gives the same result with the same basis set and geometry, see ref. 6.

geometry¹², with $R_{\text{CC}} = 1.338$ Å, $R_{\text{CH}} = 1.085$ Å, $\Theta_{\text{HCH}} = 117.8^\circ$. For the 90° twisted conformation, all the geometrical parameters were kept constant. The GVB(2/4) wave function is constructed from the C=C double bond (σ , π) pairs and has the form:

$$\Psi_{\text{C}_2\text{H}_4}^{\text{GVB}} = \mathcal{A}[\Psi_{\text{core}} \psi_{\text{C1-C2}(\sigma)} \psi_{\text{C1-C2}(\pi)}] \quad (32)$$

and the total correlation energy can be expressed as

$$\Delta E_{\text{total}} = \Delta E_{\text{C1-C2}(\sigma)} + \Delta E_{\text{C1-C2}(\pi)} \quad (33)$$

The GVB results for C₂H₄ are summarized in Table II. Our GVB(2/4) correlation energy is slightly lower than recent PS-GVB results¹² for both the planar (D_{2h}) and the twisted (D_{2d}) geometry, using the same geometry but a different basis set. However, both of the GVB(2/4) calculations give the same result (74.2 kcal/mol) for the double bond singlet rotational barrier ($D_e = E_{D_{2d}} - E_{D_{2h}}$). The GVB(6/12) calculation, which is comprised of two C1-C2 bond pairs and four C-H bond pairs, gives a singlet rotational barrier of 76.9 kcal/mol higher by 2.7 kcal/mol from the GVB(2/4) result with the same geometry. In a recent article by Goddard et al.,⁹ the one-pair GVB description of the π bond in C₂H₄ predicts the twisted structure to be higher than the planar structure by 0.317619 au, which corresponds to a singlet rotational barrier of 199 kcal/mol. This result is obviously due to a misprint or an incorrect convergence and not a failure of the one-pair GVB.

TABLE II.
Comparison of the GVB Results for C₂H₄ (Energy in Hartrees).

	HF Total Energy	GVB(2 / 4)			GVB(6 / 12)	
		Total Energy	Correlation Energy		Total Energy	Correlation Energy
			This Work	Reference ^a		
Planar (D_{2h})	−78.03797	−78.07741	−0.03944 ^b	−0.03852	−78.13618	−0.09921
Twisted (D_{2d})	−77.86080	−77.95908	−0.09828	−0.09273	−78.01352	−0.15272
Barrier (kcal / mol)	111.2	74.2 ^c	—	74.2 ^a	76.9 ^c	—

^aGoddard et al.'s PS-GVB result from ref. 12.^bComparison with Murphy's recent result.⁶ GVB-SOPP(2 / 4) gives a correlation of 0.03513 au using the bent bond description.^cThe available experimental result for a π BDE of ethylene is 64 kcal / mol.²⁹ Our GVB(2 / 4) / 6-31G** / 6-31G** calculated BDE for ethylene is 63.6 kcal / mol (cf. Fig. 3).**C₂H₆**

The GVB(7/14) calculations of C₂H₆ are carried out using the 6-31G** basis set and the experimental geometry.²³ The GVB(7/14) wave function, in which seven bond pairs are involved (one C-C and six equivalent C-H bonds), is constructed as

$$\Psi_{\text{C}_2\text{H}_6}^{\text{GVB}} = \mathcal{A}[\Psi_{\text{core}} \psi_{\text{C1-C2}} \psi_{\text{C1-H1}} \psi_{\text{C1-H2}} \psi_{\text{C1-H3}} \psi_{\text{C2-H4}} \psi_{\text{C2-H5}} \psi_{\text{C2-H6}}] \quad (34)$$

and the total correlation energy can be expressed as

$$\Delta E_{\text{total}} = 6\Delta E_{\text{C-H}} + \Delta E_{\text{C-C}} \quad (35)$$

The same geometrical parameters are used for both the staggered and eclipsed conformations.

Table III summarizes the GVB results. The rotational barrier of 3.3 kcal/mol is in good agreement with the experimental value of 2.93 kcal/mol²⁴ and the previous GVB result of 3.1 kcal/mol,^{1b} with the staggered conformation being lower in every case.

CONVERGENCE OF GVB CALCULATIONS

To demonstrate our GVB convergence, some systems are selected to represent the different GVB models, from GVB(1/2) (one pair) to GVB(10/20) (10 pairs). GVB calculations are performed with various standard Pople basis sets (STO-3G, 3-21G, 6-31G*, 6-31G**, 6-31++G**, and 6-311G**), using HF LMOs as the initial orbitals. GVB/6-31G** calculations are also performed using extended Huckel LMOs as the initial orbitals. The total energies are summarized in Table IV, and the results of

TABLE III.
Comparison of the GVB Results for C₂H₆ (Energy in Hartrees).

	HF Total Energy	GVB(7 / 14)		
		Total Energy	Correlation Energy	
			This work	Reference ^a
Staggered	−79.23631	−79.34370	−0.10739	−0.1083
Eclipsed	−79.23074	−79.33839	−0.10765	−0.1086

^aGoddard et al. results from ref. 1b.^bThe experimental result is 2.93 kcal / mol; see ref. 24.

TABLE IV.
Total RHF and GVB Energies (in Hartrees).

Molecule	Method	STO-3G	3-21G	6-31G*	6-31G**	6-31++G**	6-311G**
F ₂	RHF	-195.96743	-197.64415	-198.67382	-198.67382	-198.68095	-198.72708
	GVB(1/2)	-196.04519	-197.71926	-198.74833	-198.74833	-198.75575	-198.80378
H ₂ O	RHF	-74.96305	-75.58542	-76.01050	-76.02312	-76.03073	-76.04639
	GVB(2/4)	-75.00315	-75.62810	-76.05287	-76.06411	-76.07155	-76.08826
HNC	RHF	-91.64410	-92.33941	-92.85473	-92.85920	-92.86492	-92.88159
	GVB(2/4)	-91.68875	-92.38253	-92.89744	-92.90157	-92.90765	-92.92486
	GVB(3/6)	-91.69514	-92.39153	-92.90641	-92.91055	-92.91670	-92.93458
	GVB(4/8)	-91.70762	-92.40630	-92.92127	-92.92502	-92.93112	-92.94888
·CH ₃	RHF	-38.79604	-39.22481	-39.44614	-39.45288	-39.50648	-39.48053
	GVB(3/6)	-39.11445	-39.38276	-39.59914	-39.60375	-39.60639	-39.61251
HCCH	RHF	-75.85287	-76.39528	-76.81710	-76.82116	-76.82682	-76.84025
	GVB(2/4)	-75.91726	-76.44554	-76.86478	-76.86888	-76.87344	-76.88733
	GVB(3/6)	-75.92289	-76.45256	-76.87197	-76.87606	-76.88066	-76.89483
	GVB(5/10)	-75.94894	-76.48010	-76.89980	-76.90326	-76.90787	-76.92230
H ₂ CCH ₂	RHF	-77.07207	-77.59979	-78.03078	-78.03792	-78.04249	-78.05385
	GVB(1/2)	-77.11659	-77.63054	-78.05989	-78.06704	-78.07042	-78.08214
	GVB(2/4)	-77.12496	-77.64065	-78.07017	-78.07743	-78.08070	-78.09275
	GVB(6/12)	-77.18165	-77.69900	-78.13020	-78.13620	-78.13958	-78.15188
Glycine	RHF	-279.10589	-281.22876	-282.80827	-282.82461	-282.83455	-282.89268
	GVB(10/20)	-279.29109	-281.40577	-282.99178	-283.00605	-283.01653	-283.07487

F₂: GVB(1/2) for the F-F bond. H₂O: GVB(2/4) for two O-H bonds. HNC: GVB(2/4) for two N-C π bonds, GVB(3/6) adding an N-C σ bond, GVB(4/8) adding an H-N bond. ·CH₃: GVB(3/6) for three C-H bonds. HCCH: GVB(2/4) for two C-C π bonds, GVB(3/6) adding a C-C σ bond, GVB(5/10) adding two C-H bonds. H₂CCH₂: GVB(1/2) for the C-C π bond, GVB(2/4) adding a C-C σ bond, GVB(6/12) adding four C-H bonds. Glycine: GVB(10/20) for all 10 bonds. The experimental geometries are used,¹⁶ except for glycine (HF/STO-3G geometry).

the number of GVB iterations are reported in Table V. All the calculations are performed on the experimental geometries¹⁸ except for glycine, for which the HF/STO-3G geometry is used.

The default accuracy for all convergence criteria (ρ_{orb} , ρ_c and ρ_d) is 10^{-5} . In ref. 9, Goddard et al. used the SQCDF ($\leq 10^{-9}$) as the convergence criterion which is related to our orbital coefficients' convergence accuracy ρ_c :

$$\text{SQCDF} = \rho_c^2 \times N_{\text{basis}} \times N_{\text{occ}} \quad (36)$$

In most cases for moderate-size molecules, $N_{\text{basis}} \times N_{\text{occ}} \approx 10^3$, so that $\rho_c \leq 10^{-5}$ is equivalent to $\text{SQCDF} \leq 10^{-7}$. As pointed out, the density convergence accuracy ρ_d is a better criterion since it incorporates all GVB variational parameters.

The correlation energy calculated with our GVB wave function is consistent with other GVB calculations, as discussed earlier. Generally, there is only a small effect due to polarization or diffuse functions on the GVB-PP correlation energy. For example, the correlation energy calculated for the

F-F σ bond in F₂ [GVB(1/2)] and for the two O-H σ bonds in H₂O [GVB(2/4)] is ~ 0.075 au and ~ 0.042 au, respectively, approximately the same for all basis sets considered. GVB(5/10) for all bonds in HCCH gives the correlation energy of ~ 0.082 au, with the π bond contribution of ~ 0.047 au [GVB(2/4)] and the σ contribution of ~ 0.035 au ([GVB(5/10) - GVB(2/4)]). GVB(10/20) for all bonds of glycine gives a correlation energy of ~ 0.182 au.

As in DIIS-GVB,⁹ reliable convergence requires a reliable initial guess to ensure that the starting point is within the radius of convergence. Our GVB procedure gives a similar convergence, once a reliable guess is obtained. The GVB(2/4)/6-31G** calculation of C₂H₄ converges at seven iterations, for instance, compared to 10, 15, and 26 iterations for the corresponding GVB-DIIS, GVB2P5, and G90, respectively.⁹ For glycine, our GVB(10/20)/6-31G** converges at 16 iterations, compared to 20, 90, and 75 iterations for the corresponding GVB-DIIS, GVB2P5, and G90, respectively.⁹ The GVB/6-31G** calculations using the

TABLE V.
Numbers of Iterations for Converging GVB Calculations.

Molecule	Method*	STO-3G	3-21G	6-31G*	6-31G**		6-31++G**	6-311G**	Reference
					HMO ^a				
F ₂	GVB(1 / 2)	10	16	9	9	8	9	15	14 ^b 24 ^c , 89 ^d
H ₂ O	GVB(2 / 4)	8	14	10	10	15	11	14	
HNC	GVB(2 / 4)	8	9	8	9	11	9	12	
·CH ₃	GVB(3 / 6)	8	12	8	9	12	9	14	14 ^b 17 ^c , 28 ^d
	GVB(4 / 8)	8	11	8	9	13	9	20	
	GVB(3 / 6)	11	12	12	11	14	13	16	
HCCH	GVB(2 / 4)	6	8	7	7	9	8	8	10 ^b 15 ^c , 26 ^d
	GVB(3 / 6)	7	8	8	7		7	10	
	GVB(5 / 10)	6	9	8	8		8	9	
H ₂ CCH ₂	GVB(1 / 2)	4	11	7	7	10	8	7	20 ^b 90 ^c , 75 ^d
	GVB(2 / 4)	5	13	9	9	12	9	8	
Glycine	GVB(6 / 12)	4	13	9	9	9	10	10	20 ^b 90 ^c , 75 ^d
	GVB(10 / 20)	12	20	14	16		10	18	

*See notes for Table IV.

^aThe initial orbitals are from extended Huckel LMOs, whereas the initial orbitals are from HF LMOs for all other cases.^bGVB-DIIS.⁴^cGVB2P5.⁴^dG90.⁴

extended Huckel LMO guess generally converge as well as for the HF LMO guess. Overall, our GVB converges within 10 to 20 iterations (Table V), demonstrating that the GVB method as described earlier provides excellent convergence for a wide variety of wave functions based on reliable initial orbitals, which are generated automatically. Further improvements in convergence should be possible by incorporating the DIIS method to our GVB.

σ AND π BOND DISSOCIATION

The GVB(2/4) calculation is performed with the optimized minimum at 6-31G**, then keeping C_s symmetry to dissociate the O-H1 bond, with the O-H2 bond length and H1-O-H2 bond angle fixed. The GVB(2/4)/6-31G** potential curve for the H₂O → HO· + H· dissociation is shown in Figure 2. The resulting bond dissociation energy (BDE, D_e) is 100.5 kcal/mol, compared with the available experimental result of D_e = 126 kcal/mol.²⁵ The reported HF limit is 89 kcal/mol at 6-31G**, and 116 kcal/mol at MP4/6-31G**.²⁶ The GVB(4/8) result of 101.3 kcal/mol shows that oxygen lone pairs have little effects on the O-H BDE in our

GVB calculation. The bond-breaking process can be described reasonably well even with such a simple wave function consisting of an independent GVB bond pair.

Figure 3 illustrates the GVB(2/4)/6-31G** potential curve for the rotation about the C=C double bond of C₂H₄. The GVB(2/4)/6-31G** calculation is carried out with rigid rotation about the C=C bond. The 63.6 kcal/mol barrier for singlet rotation around C=C double bond is consistent with the previous CI result of 61 kcal/mol,²⁷ the GVB result of 65 kcal/mol,²⁸ and the experimental result of 64 kcal/mol.²⁹

Conclusions

1. The generation of GVB-PP orbitals for specific chemical bonds has obvious computational and conceptual advantages and results in the automatic generation of reliable initial orbitals.
2. Boys's localized molecular orbitals are good starting orbitals for GVB calculations.
3. The pairwise orbital optimization procedure gives reliable and fast convergence. The GVB

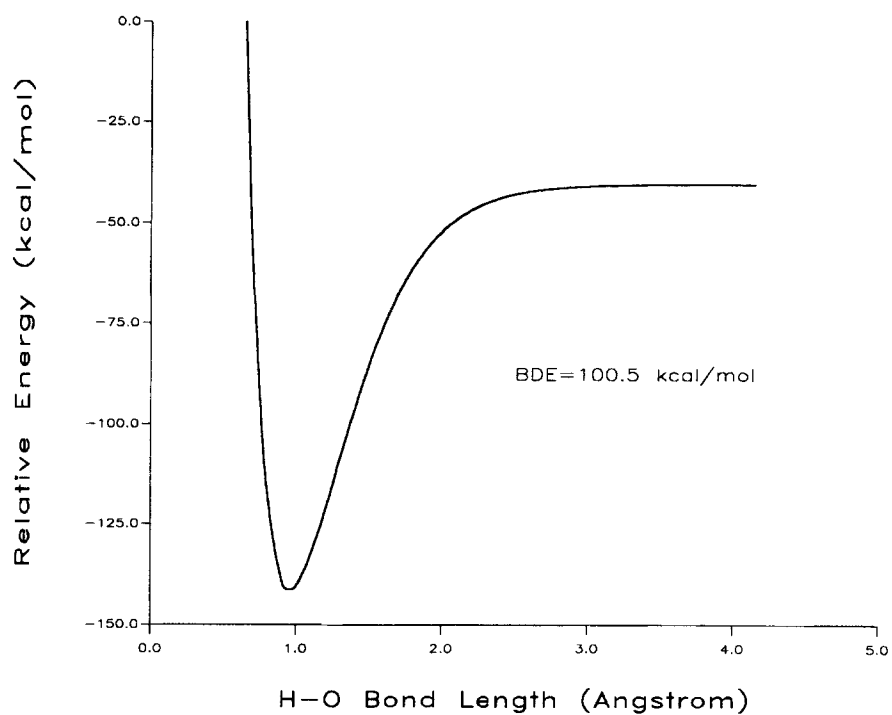


FIGURE 2. The potential energy curve for $\text{H}_2\text{O} \rightarrow \text{HO} \cdot + \cdot\text{H}$.

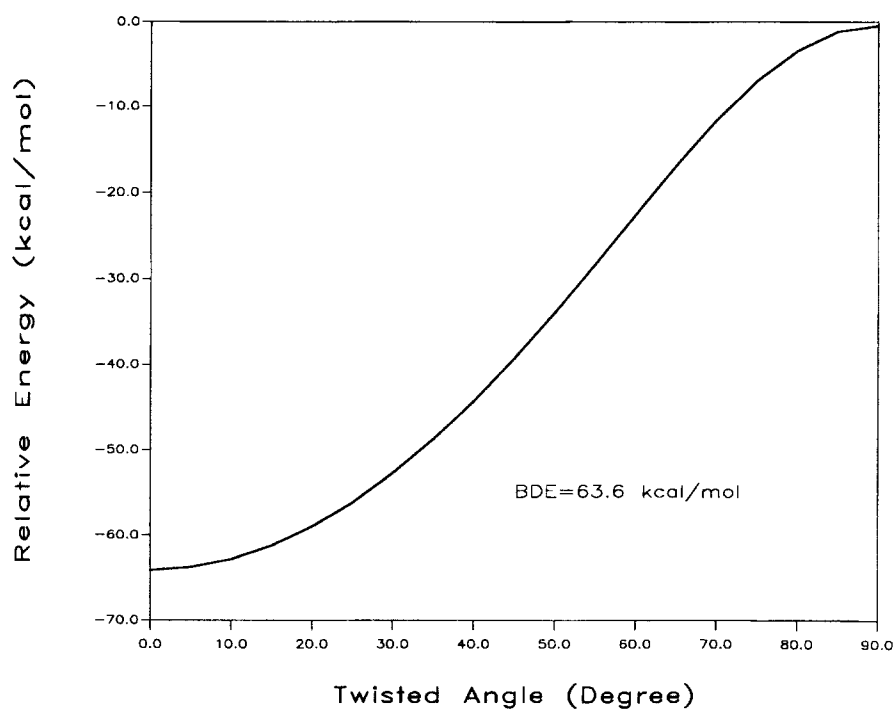


FIGURE 3. The potential energy curve for C=C double bond singlet rotation in C_2H_4 .

generally converges within 10 to 20 iterations for all molecules examined using different basis sets and GVB pairs. The algorithms described in this work can also be applied to MCSCF calculations.

3. Since the initial orbitals are localized, our approach provides a simple, adequate, and consistent description of the potential energy surface. BDEs calculated at optimized GVB geometries are in reasonable agreement with the experimental values.

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